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(54) Abstract Title
Dishwasher tablets

(57) A detergent tablet product for use in an automatic washing machine is comprised of a tablet within a water soluble wrapping. The tablet comprises first and second water soluble layers which are such that the former dissolved more rapidly than the latter under identical dissolution conditions.

Methods of producing detergent tablets having differentially soluble first and second layers are described and involve co-compressing a first layer comprised of a light granular builder and a second layer comprised of a dense powder builder.

The tablets may comprise differentially soluble first and second layers in which the first layer incorporates an enzyme and a bleach and the second layer incorporates an activator for the bleach.

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DISHWASHER TABLETS

The present invention relates to detergent tablets for use in automatic dishwashing machines.

Tablets for automatic dishwashing machines have been known for a number of years in the Industrial and Institutional sector and conventionally contain caustic alkali and chlorine bleaches for cleaning effect. Such tablets are usually made by either drying a slurry of ingredients or allowing the slurry to set by hydration. More recently tablets have been produced for domestic use. and for a number of reasons. one of which is the safety of the domestic user, generally contain milder chemical cleaning components such as enzymes and oxygen based bleaches. These tablets for domestic use are conventionally produced by compressing a powdery or granular mix of ingredients on a tableting press.

A potential problem in the formulation of such tablets is that some ingredients are mutually incompatible. A prime example is the previously mentioned enzymes and chlorine or activated oxygen based bleaches where significant deactivation of enzymes can occur thus reducing enzymatic cleaning effect and causing bleach to be consumed. This problem can occur during storage and also when the tablet is dissolved in the wash liquor. The problems of undesirable interaction between mutually incompatible first and second components (e.g. an enzyme and a bleach) of a tablet such as may occur during storage of the tablet may be avoided or mitigated by segregating the components from each other. Furthermore, in the case where one of the incompatible components is required earlier in the wash cycle than the other (e.g. an enzyme may be required earlier than a bleach) problems with undesirable interactions in the wash liquor may be reduced by ensuring that the former component (or a proportion thereof) is released earlier that the latter component (as a proportion thereof). This may be achieved in a number of ways.

Firstly, the incompatible ingredients may be provided in separate concentric layers. so that the release of the incompatible ingredients is bound to be sequential. For example, the enzymes could be placed in an outer layer, allowing the enzymes to work before the bleach is released from the core of the tablet. A problem with this approach is that it is difficult to manufacture such tablets on a tablet press, the concentric structure being suited to the slurry casting method mentioned above. While this method is suitable for low volume manufacture where individual tablets can be several kilograms it is unsuitable for high volume domestic auto dish wash tablet manufacture where the individual tablet weight is typically about 20 grams.

Secondly, the delayed dissolution of one or more of the incompatible components may be achieved by coating one or more of the incompatible ingredients in a hydrophobic substance in order to retard dissolution. The problem with using such coated ingredients is that these have to be specially manufactured usually incurring extra expense compared to the conventional ingredient.

Thirdly, the tablet may comprise first and second differentially soluble layers co-compressed together in face-to-face relationship whereby one layer dissolves more rapidly in water than the other under identical dissolution conditions. The (incompatible) component which is to be delivered relatively early in the wash cycle is incorporated in the more rapidly dissolving layer whereas that component which is to be delivered relatively late in the wash cycle is incorporated in the slower dissolving layer.

The tablets as described in the previous paragraph are such that they are ideally used

(a) in dishwashing machines which do not utilise a cold water prewash. or

(b) if used in a machine which does utilise a prewash, the tablets are placed in the drawer (of the machine) which does not open until the main wash cycle begins.

If however the tablets are placed directly in the dish compartment of an automatic dishwashing machine which utilises a cold water prewash then (depending on the actual formulation of the tablet) problems could arise with the first layer dissolving during the prewash. This would mean that the components originally present in the first layer would not be delivered to the main wash cycle.

According to a first aspect of the present invention there is provided a detergent tablet product for use in an automatic dishwashing machine, the product incorporating a tablet comprising first and second water soluble layers which are such that the former dissolves more rapidly than the latter under identical dissolution conditions, wherein said tablet is provided with a water soluble wrapping.

Preferably the film is only breached at the beginning, or during the early stages, of the wash cycle.

It is particularly preferred that the film is one which has a breach time of 10 to 300 seconds in the test as outlined in the following paragraph.

These breach times have a number of advantages. Firstly, the film will be able substantially to protect the first layer against substantial dissolution during a pre-wash stage. Secondly, the breach time may allow some breach of the wrapping to occur during the pre-wash to allow limited dissolution of the first layer and deliver active components during the pre-wash. Thirdly, in the event that a dishwashing machine is operated without a pre-wash cycle, the breach times are such that tablet dissolution is able to commence before too long into the main cycle.

The test utilises a cylindrical bottle having a height of 6 cm and an internal diameter of 25 mm. For the purpose of the test, the bottle is half filled with water at 20°C and 290 ppm calcium carbonate. The water soluble film to be tested is securely placed over the end of the cylindrical bottle which is then inverted. The time for the

film to rupture and release water is defined as the breach time. This test is also referred to herein as a test of the kind defined.

Preferably the breach time is 20 to 120 seconds, more preferably 20 to 100 seconds, even more preferably 30 to 80 seconds, still more preferably 30 to 60 seconds and ideally about 50 seconds.

A suitable material for the water-soluble wrapping is polyvinyl acetate which has optionally been at least partially hydrolysed to polyvinyl alcohol (PVA). The required solubility for the wrapping (i.e. so that it remains intact during the cold water prewash) may be achieved by varying factors such as the degree of hydrolysis and/or the thickness of the wrapping. These parameters may readily be adjusted by those skilled in the art to achieve a wrapping material which meets the desired requirements.

Other suitable polymers for use as the wrapping include poly vinyl pyrrolidine, poly acrylic acid, poly acrylate maleate, poly acrylamide, poly cellulose ethers, polyethylene copolymers and mixtures thereof.

The wrapping may for example be of polyvinyl acetate having a degree of hydrolysis in the range 0% to 100%, preferably 50% to 100%, more preferably 50% to 90%, and most preferably 75% to 85%. The degree of hydrolysis may be about 80%.

The thickness of the film may for example be 10 to 500μm, more preferably 30 to 200μm and most preferably 35 to 60μm.

We have found that a further advantage of using a water soluble film is that the dissolved film material serves as a rinse-aid therefore giving the possibility of reducing, or eliminating, the amount of a rinse aid which might otherwise preferably be employed in the tablet.

As stated, the first and second layers are differentially soluble so that the former dissolves more rapidly than the latter in water under identical dissolution conditions. Thus components which are to be delivered relatively early in the wash cycle may be incorporated in the first layer whereas components to be delivered later in the cycle may be incorporated in the second layer. It should however be appreciated that the tablets may be such that a proportion of the components to be delivered from the second layer are released into the wash liquor before complete dissolution of the first layer. However, the important feature of the tablet is that the components from the first layer will be released before the major part of the components from the second layer.

The first layer may, for example, incorporate an enzyme for delivery during an early part of the wash cycle and the second layer may, for example, incorporate a bleach. More detailed examples of such components are given below. In addition to such components the tablet will comprise components such as a surface active agent, (e.g. provided in at least the second layer), and components such as soil suspension agents, anti-corrosion agents, a source of alkalinity, and/or crystal growth inhibitor. Specific examples of such components are given hereinafter.

Each of the first and second layers will also incorporate a builder. The builder of any one layer may for example, be an alkali metal polyphosphate, an alkali metal carbonate, alkali metal bicarbonate, alkali metal citrate, zeolite or a crystalline or amorphous silicate builder system. Mixtures of these builder systems can be used.

It is preferred (but not essential) that the builders of the two layers are chemically the same.

It is particularly preferred that the builder of each layer is sodium tripolyphosphate.

The differential solubility of the first and second layers may be achieved by co-compressing a first layer formulated to be compressed of a light granular builder and other components for that layer, and a second layer comprised of a dense powdery builder and the other components of that layer.

This is an important aspect of the invention in its own right and therefore according to a second aspect of the present invention there is provided a method of producing a detergent tablet comprising co-compressing a first layer comprised of a light granular builder and a second layer comprised of a dense powdery builder to produce a tablet in which the first layer dissolves more rapidly in water than the second layer under identical dissolution conditions.

This second aspect of the invention has been based on our finding that detergent tablets having layers of differential solubility may readily be produced by formulating one layer with a light granular builder and the other with a dense powdery builder, and co-compressing the two layers (e.g. using a conventional tableting press). Without wishing to be bound by theory, it is believed that the increased compressibility of a light granular builder (as compared to a dense powdery builder) allows a tablet sufficient mechanical strength to be pressed with a lower degree of fusion between the granules thus allowing faster dissolution.

It is preferred that the builder of the first layer in its pre-compressed granular form has a bulk density of less than 0.8 g/cc and a granulometry such that at least 30% by weight would be retained on a 500 micron sieve and at least 15% by weight would be retained on a 710 micron sieve. More preferably, this bulk density is less than 0.7 g/cc and the granulometry is such that at least 40% by weight would be retained on a 500 micron sieve and at least 25% by weight on a 710 micron sieve. Even more preferably, this bulk density is less than 0.6 g/cc and the granulometry is such that at least 40% by weight would be retained on a 500 micron sieve and at least 25% by weight would be retained on a 710 micron sieve.

The builder of the second layer is preferably such that, in its pre-compressed granular form, it has a bulk density greater than 0.8 g/cc and a granulometry such that less than 50% by weight would be retained on a 500 micron sieve and less than 30% by weight would be retained on a 710 micron sieve. More preferably this bulk density is greater than 0.9 g/cc and the granulometry is such that less than 40% by weight would be retained on a 500 micron sieve and less than 20% by weight would be retained on a 710 micron sieve. Even more preferably this bulk density is greater than 1.0 g/cc and the granulometry is such that less than 40% by weight would be retained on a 500 micron sieve and less than 20% by weight would be retained on a 710 micron sieve.

The builder of any one layer may, for example, be an alkali metal polyphosphate, an alkali metal carbonate, alkali metal bicarbonate, alkali metal citrate, zeolite or a crystalline or amorphous silicate builder system. Mixtures of these builder systems may be used.

It is preferred (but not essential) that the builders of the two layers are chemically the same.

It is particularly preferred that the builder of each layer is sodium tripolyphosphate. The sodium tripolyphosphate for the first layer (i.e. the layer which dissolves more quickly) may for example be STP GL (ex Kemira Chemie) or STP PC (ex Albright and Wilson) whereas that for the second layer may be STP P (ex Albright and Wilson).

To produce the tablets, the formulations for the first and second layers are produced separately and then introduced as separate layers into the die of a tableting press and co-compressed.

A pressure of 20 to 500 MPa will generally be suitable for forming the tablet. More preferably, a pressure of 50 to 350 MPa is used and even more preferably one of 80 to 200 MPa.

There are a number of models of tableting press which are capable of producing dual layer tablets, for instance the "Excelapress" and "Rotapress" models are produced by BWI Manesty of Liverpool. It is also possible to modify a single layer press to produce dual layer tablets, for instance an RS model, also ex Manesty, could be modified in this way.

Tableting presses generally work by having a rotating circular turret with arrays of punches which compress the tablets from above and below. The cycle consists of filling the die with the powder which will make up one of the layers, followed by filling with the powder of the second layer, compression of the tablet, and release.

Machines specially designed for dual layer operation usually have a small amount of pre-compression between filling the die with the powders of the first and second layers. This gives a sharper definition between the two layers which may be more aesthetically pleasing, particularly if the layers are of different colours.

The tableting press should be equipped with a feed mechanism so that the two powders are fed into the die in the weight ratio desired. Excess powder is removed from the area of the die by means of scrapers. The press should allow the tablet thickness to be adjustable. For a given die/punch size, this allows the tablet weight to be regulated.

The press should also have a control to regulate the applied force used in the main compression. The applied pressure should typically be about 20 to 500 MPa, which for a 20 gram tablet would translate to an applied force per tablet of about 18 to 450 kN. The pressure applied is a crucial part of the tableting operation as inadequate

pressure will give a tablet which is not robust enough to withstand handling, while excess pressure gives a tablet which dissolves too slowly. The tablet strength may be monitored by use of equipment to measure its breaking strength under compression, such as the Holland CT5 automatic compression tester. The tablet is placed so that its smallest two opposite faces are placed between the compression bars. A 20 gram tablet should break at about 15-150 kg applied force, which corresponds to about 500-5000 kPa.

It is preferred that, in water at a temperature of 55°C to 65°C, the first layer of the tablet (of the first or second aspect of the invention) dissolves at least twice as rapidly as that of the second layer. More preferably, under the same conditions, the first layer dissolves at least three times as quickly as that of the second layer and ideally not more than four times as quickly. The rates at which the first and second layers in a tablet produced under particular conditions will dissolve may be determined by producing (under the same conditions) test tablets which are comprised of

(a) only the formulation of the first layer, and.
(b) only the formulation of the second layer.

The relative rates at which the two tablets dissolve (e.g. as measured by weight loss over time) in water at the same temperature can then be measured easily. As indicated. it is preferred that the formulation of the first layer dissolves at least twice as quickly as that of the second layer.

Ideally the first layer dissolves within 5 minutes and the second layer within 20 minutes.

The relative amounts of the first and second layers in the tablet may be in the range 1:10 to 10:1. preferably 5:1 to 1:5. and more preferably 2:1 to 1:2.

Tablets produced in accordance with the first or second aspects of the invention will generally consist of only the first and second layers as discussed above although we do not preclude the possibility of additional layers being present. The tablet may for example comprise the second layer sandwiched between two of the first layers. Each of the first and second layers will, in the depth dimension of the tablet, generally have a thickness considerably less than the other two dimensions so that in a two layer tablet the individual layers have major faces in juxtaposed face-to-face relationship. The first and second layers may, for example, have a major face of circular or rectangular shape. The tablet may typically weight about 20g and if desired the first and second layers may be differently coloured.

It is particularly preferred in accordance with the first and second aspects of the invention that the first layer incorporates at least one enzyme to be delivered during the early part of the wash cycle. It is also preferred that the second layer incorporates a bleaching system. In a further embodiment of the invention it is preferred that the first layer incorporates an enzyme and a bleach and that the second layer incorporates a bleach activator and possibly also further bleach. Such tablets comprise an important aspect of the present invention in their own right and therefore according a third aspect of the present invention there is provided a pressed detergent tablet for use in an automatic dishwashing machine, the tablet comprising first and second water soluble layers which are such that the former dissolves more rapidly in water than the latter under identical dissolution conditions wherein the first layer incorporates an enzyme and a bleach and the second layer incorporates an activator for the bleach optionally with further bleach.

Tablets in accordance with the third aspect of the invention have the advantage that, because at least a proportion of the total bleach is provided in the first layer, that layer is bulkier (and thus has a larger surface area) than would be the case if all of the bleach were provided in the second layer. This increased surface area facilitates more rapid dissolution of the first layer as compared to the second layer.

Tablets in accordance with the third aspect of the invention (which may be produced by the method of the second aspect of the invention) are therefore suitable for delivering an enzyme to the (relatively low temperature) wash liquor during an early part of the main wash cycle and an activated bleach during a later, higher temperature part of the cycle. Given that the activated bleach system is one which would destroy the activity of the enzyme, it is thus possible to use such tablets to deliver an enzyme to the wash liquor during an early part of the cycle so that the enzyme may act before it is degraded by the activated bleaching system.

We have found that the enzymes of the first layer will tolerate the presence therein of the bleach (usually a hydrogen peroxide precursor compound (e.g. a perborate)) without problems of storage stability and without degrading activity of the enzyme during the wash cycle. Consequently tablets in accordance with the invention may have a first layer incorporating at least one enzyme and a hydrogen peroxide precursor compound and a second layer incorporating a bleaching activator, the bleach and the activator together providing an activated bleaching system. The incorporation of a hydrogen peroxide precursor in the first layer will, in fact, have the advantage that hydrogen peroxide will be present in the wash liquor at the time that the bleach activator is subsequently released from the second layer. This can be advantageous in that the bleach activator may be able to generate the active bleaching species earlier than would be the case for simple dissolution of the activated bleaching system from the second layer.

The activated bleaching system for use in any aspect of the invention may comprise a compound which generates hydrogen peroxide on dissolution in water together with a bleach activator. The hydrogen peroxide compound may, for example, be an inorganic persalt, e.g. a perborate (in the monohydrate and/or tetrahydrate form), a percarbonate or a persulphate. The alkali metal salts of these compounds are preferred, particularly sodium and potassium salts. The bleach activator may be a compound incorporating aliphatic acyl groups preferably having two or three carbon atoms, the acetyl group being preferred. Examples of suitable bleach activators are

tetraacetylethylene diamine (TAED) and acetylated polyols such as acetylated sugars (e.g. penta acetyl glucose, fractose etc.) and acetylated sugar derivatives (e.g. acetylated sorbitol and acetylated mannitol). All of these specific bleach activators are capable of reacting with hydrogen peroxide to generate peracetic acid as an active bleaching species.

The enzyme for use in any aspect of the invention may for example be a protease, an amylase, an oxidase, peroxidase or lipase (or mixtures thereof). Examples of suitable enzymes are available under the names Savinase, Esperase (a protease), Termamyl (an amylase), and Guardzyme (a peroxidase) (all ex Novo Nordisk); Maxamyl (an amylase), Maxacal and Purafect (both proteases) and Lipolase (a lipase) (all ex Genencor International); Peroxidase and Laccase (an oxidase) (both generic names).

The tablet will comprise a surface active agent such as conventionally used for automatic dishwashing formulations. Generally the surface active agent will be incorporated in the second layer. Alternatively or additionally either of the layers may include a surface active agent. It is particularly preferred that the surface active agents employed in the tablets are non-ionic surface active agents such as available under the trade name Synperonic. Further examples of surfactants which may be used include Lutensol A03 or A07 (ex BASF), Plurafac, LF404 or LF244 (ex BASF) or Dobanol 91-7 or 91-3 (ex Shell).

Further ingredients which may be present in one or both of the first and second layers include

(i) soil suspension agents (e.g. disilicate)
(ii) anti-corrosion agent (e.g. disilicate)
(iii) source of alkalinity (e.g. sodium carbonate)
(iv) crystal growth inhibitors (e.g. a phosphonate)
(v) anti-tarnishing agents (e.g. benzatriazole).

(vi) bleach scavengers (e.g. ammonium sulphate, sodium, potassium or ammonium glutamate or sodium or potassium bisulfite).

(vii) water softening agents (e.g. a phosphate or polycarboxylate)

(viii) fat emulsifier (e.g. a non-ionic surfactant)

(ix) binder (e.g. ethylene glycol)

(x) perfume

(xi) dye

Each of the first and second layers may, for example, comprise

Builder (e.g. phosphate, carbonate and/or sulphate)	[1]10% to 80%
Hydrogen Peroxide Precursor Compound	5% to 20%
Surfactant	up to 5%
Soap	0% to 4%
Phosphonate	0.1% to 3%
Polymer	0% to 4%
Perfume	0% to 3%
Corrosion Inhibitor	0.01% to 1%

[1]10% to 90% of at least a portion of the builder is provided by silicate.

If the first layer contains an enzyme then the amount thereof may for example be 0.1% to 3% by weight (of the first layer) for each enzyme type (e.g. protease, amylase, cellulase). If the second layer contains bleach activator then the amount thereof may for example be 1% to 6% by weight of the second layer.

In order to overcome this problem it is proposed in a further embodiment of either the first or second aspect of the invention that the tablet be provided within a water-soluble wrapping (e.g. a sachet) which maintains its integrity for at least part of the cold water prewash before the film is breached to expose the tablet for dissolution as discussed above.

The invention is illustrated by the following non-limiting Examples.

Example 1

Four formulations were prepared in accordance with the following table (each formulation differing only in the type of sodium tripolyphosphate (STP) used):

Table 1

RAW MATERIAL	STP P VARIANT	STP PC VARIANT	STP GL VARIANT	STP L16 VARIANT
STP	47.00%	47.00%	47.00%	47.00%
PYRAMID G80 (Sodium Silicate ex Crosfields)	25.00%	25.00%	25.00%	25.00%
GRAN ASH (Sodium Carbonate)	5.52%	5.52%	5.52%	5.52%
SODIUM PERBORATE (TETRAHYDRATE)	12.00%	12.00%	12.00%	12.00%
ESPERASE 4.0T (Protease Enzyme)	2.25%	2.25%	2.25%	2.25%
TERMAMYL 6.0T (Amylase Enzyme)	2.25%	2.25%	2.25%	2.25%
DEQUEST 2016D EX MONSANTO	0.40%	0.40%	0.40%	0.40%
BENZATRIAZOLE	0.40%	0.40%	0.40%	0.40%
PALM SOAP	0.19%	0.19%	0.19%	0.19%
PEG (MW 2000)	0.19%	0.19%	0.19%	0.19%
SILICONE ANTIFOAM (Poly Dimethyl Siloxane)	0.10%	0.10%	0.10%	0.10%
SYPERONIC LFRA 260 (ex ICI)	3.00%	3.00%	3.00%	3.00%

The granulometry and bulk density of the various sodium tripolyphosphates used in the above formulations are shown in Table 2 below.

Table 2

STP grade in Layer	wt% retained on sieve mesh (cumulative)		Bulk Density (g/cc
	210 micron	500 micron	
PC	27.80	51.40	1.18
GL	23.10	44.90	0.50
L16	8.00	19.00	0.60
P	18.20	36.30	1.08

Each of the formulations in Table 1 was pressed into tablet form on a conventional tableting press using approximately 6 tonne of pressure.

The tablets were weighed and dissolution rate measured by placing a tablet in the dispensing drawer of Bosch dishwasher (model SMS 5032913 4). initiating the 55° quick wash cycle. stopping the cycle every two minutes. and re-weighing the tablet. This test was carried out for two tablets of each formulation and the results are shown in Table 3.

Table 3

TIME	STP P VARIANT		STP PC VARIANT		STP GL VARIANT		STP L16 VARIANT	
START	19.60	19.70	19.80	19.70	19.90	19.80	19.80	19.85
2 MINUTES	19.60	19.70	19.80	19.70	19.90	19.80	19.80	19.85
4 MINUTES	18.00	18.40	17.60	18.2	20.80	20.10	19.52	19.32
6 MINUTES	13.90	13.10	3.50	7.80	3.60	4.40	15.00	16.90
8 MINUTES	8.40	7.50	0.00	0.00	0.00	0.00	3.60	1.60
10 MINUTES	3.70	4.00					0.00	0.00
12 MINUTES	1.90	1.60						
14 MINUTES	0.50	0.40						
16 MINUTES	0.20	0.10						
18 MINUTES	0.00	0.00						

This example demonstrates that the STP variants GL and PC are eminently suitable for use in manufacturing the first layer of the tablets of the invention whereas STP P is suitable for use in formulating the second layer. The STP L16 Variant may also be used for forming the first layer.

Tablets as produced in accordance with this Example may be enclosed within a water-soluble wrapping as described for the first aspect of the invention (see also Examples 3 and 4)

Example 2

A tablet (Table 1) was prepared having the composition shown in Table 4.

Table 4

SODIUM TRIPOLYPHOSPHATE GL	37.500
SODIUM DISILICATE HEAVY GRAN	25.000
GRANULAR SODIUM CARBONATE	7.350
SODIUM PERBORATE	12.000
ESPERASE 4.0T (Protease enzyme)	1.600
TERMAMYL 60T (Amylase enzyme)	0.750
DEQUEST 2016D	0.400
BENZOTRAIZOLE	0.200
TREPALBE SOAP	0.010
POLYETHYLENE GLYCOL	0.190
TAED (Tetra Acetyl Ethylene Diamine)	2.000
SODIUM TRIPHOSPHATE BLUE BEADS	10.000
SYNPERONIC LFRA 260	3.000

Further tablets (Tablets 2-4) were produced as modifications of the above formulation omitting one or other of perborate, TAED and Enzyme. Any omitted component was replaced by an equivalent amount of the sodium carbonate.

A summary of Tablets 1-4 is given in Table 5 below.

Table 5

Tablet Number	Perborate	TAED	Enzyme
1	Yes	Yes	Yes
2	Yes	No	Yes
3	No	Yes	Yes
4	Yes	Yes	No

They were stored for 10 days at 40°C and 90% relative humidity to determine storage stability. The amounts of perborate, protease enzyme and TAED remaining in the tablets was then assayed and the results are shown below.

% Perborate (initial 12.0%)

Tablet 1	Tablet 2	Tablet 3	Tablet 4
10.09	13.27	-	11.17

%Protease enzyme (initial 2.25%)

Tablet 1	Tablet 2	Tablet 3	Tablet 4
0.69	1.03	0.69	-

% TAED (initial 2%)

Tablet 1	Tablet 2	Tablet 3	Tablet 4
0.50%	-	1.7%	0.51%

The tables show the amounts of perborate, enzyme activity and TAED remaining the tablet after the storage period.

It will be seen from these tables that a tablet comprising enzyme and perborate but no bleach activator (i.e. Tablet 2 above) and tablets comprising perborate and bleach activator (i.e. Tablet 4 above) both have adequate storage stability. Thus it is possible to produce two layer tablets for which the first layer comprises enzyme and perborate (but no bleach activator) and the second layer comprises perborate and bleach activator.

Tablets as produced in accordance with this Example may be enclosed within a water-soluble wrapping as described for the first aspect of the invention (see also Examples 3 and 4).

Example 3

A series of 60 μm thick films were prepared from 97 parts by weight (partially) hydrolised polyvinyl acetate and 13 parts by weight glycerol. The films differed in the degree of hydrolysis of the polyvinyl acetate.

The "breach times" of the films were measured using the test of the kind defined. The results are shown in Table 6 in which the composition of the film is expressed in parts by weight of its vinyl alcohol, vinyl acetate and glycerol contents.

Table 6

Film No.	Vinyl Alcohol	Vinyl Acetate	Glycerol Plasticiser	Break time (seconds)
1	87	0	13	11
2	68.5	18.5	13	53
3	42	45	13	103
4	22	65	13	198

The above films are suitable for use in accordance with the first aspect of the invention, Film No. 2 being particularly preferred.

A suitable (polyvinyl alcohol)/(polyvinyl acetate) polymer for use in producing Film No. 2 is available from Aquafilm under the designation L337E.

Example 4

A series of films of different thickness were prepared from a (polyvinyl acetate)/(polyvinyl alcohol) polymer obtained by 80% hydrolysis of a polyvinyl acetate. The films also contained 13% by weight glycerol as a plasticiser The breach time of the film were measured using the test of the kind defined. The results are shown in table 7.

Table 7

Film No.	Thickness (μm)	Breach Time (Seconds)
5	450	600
6	310	440
7	100	131
8	50	58
9	37	37
10	25	12

Film Nos. 7-9 are suitable for use in accordance with the first aspect of the present invention. Suitable polymers for preparing films 5 to 10 are available from Aquafilm UK Ltd under the designation 97541-1 respectively.

Example 5

Two formulations A and B were produced as follows:

Formulation A

Component	**% by weight**
Sodium Tripolyphosphate	47.000
Sodium Disilicate Heavy Gran	25.000
Granular Sodium Carbonate	8.400
Sodium Perborate	12.500
Dequest 2016D	0.400
Benzotriazole	0.200
Polyethylene Glycol	0.200
TAED	3.000
Synperonic LFRA 260	3.000
Perfume	0.300

Formulation B

Component	% by weight
Sodium Tripolyphosphate GL	47.000
Sodium Disilicate Heavy Gran	25.000
Granular Sodium Carbonate	5.800
Sodium Perborate	12.500
Esperase 4.0T	2.250
Termamyl 60T	2.250
Dequest 2016D	0.400
Benzotriazole	0.200
Polyethylene Glycol	0.200
Blue Dye (Polar Blue Rawl)	0.400
Synperonic A7	3.000
Water	1.000

A conventional tableting press was used to produce dual layer tablets for which formulation B above provided the first ("quick dissolving" layer) and formulation A provided the second layer. The weight ratio of the quick dissolving layer to the slow dissolving layer (i.e. B:A) was 1:2. A pressure of 150 MPa was used to produce the tablet.

Certain of the dual-layer tablets were then provided with a wrapping of a water soluble film (50μm) of polyvinyl acetate which had been 80% hydrolysed to polyvinyl alcohol.

Further ("single-layer", unwrapped) tablets were produced from an intimate admixture of Formulations A and B).

Wrapped and unwrapped tablets were tested in a dishwashing machine utilising a cold water pre-wash cycle (15 minutes total including 5 minutes pumping out water) prior to the main wash which involved heating to 65°C.

The wash liquor was analysed for amounts of enzyme, hydrogen peroxide (expressed as perborate) and TAED at various times during the pre-wash and main wash cycles. The results are shown in the following Table.

Time(mins)	Dual layer (unwrapped)			Single layer (unwrapped)			Dual layer (wrapped)		
	% Enzyme	% TAED	%Perborate	%Enzyme	%TAED	%Perborate	%Enzyme	%TAED	%Perborate
0.0	0%	0%	0%	0%	0%	0%	0%	0%	0%
0.5	16%	0%	8%	0%	8%	7%	0%	0%	0%
2.5	19%	4%	12%	4%	11%	11%	0%	0%	0%
5.0	36%	7%	23%	7%	24%	21%	1%	1%	2%
10.0	85%	10%	50%	10%	48%	47%	5%	2%	3%
15.01	0%	0%	0%	0%	0%	0%	0%	0%	0%
15.5	3%	5%	6%	5%	6%	6%	16%	5%	12%
17.5	14%	29%	32%	29%	32%	32%	87%	31%	63%
20	15%	54%	42%	54%	43%	42%	95%	59%	82%
25	15%	71%	47%	71%	48%	47%	95%	77%	91%
30	13%	90%	50%	81%	52%	50%	86%	90%	97%
35	12%	83%	45%	70%	47%	45%	74%	98%	86%
40	7%	76%	36%	46%	35%	36%	48%	89%	69
45	4%	76%	29%	25%	28%	29%	26%	83%	57%
55	3%	75%	25%	18%	26%	22%	19%	82%	53%
75	2%	74%	23%	11%	23%	12%	12%	80%	48%
[1]Total Activity	9.5	44.85	22.5	21.33	22.71	19.8	25.1	48.3	38.5

[1]time activity arbitrary units

The results in the above table show that the unwrapped dual layer tablet looses much of its enzyme effectiveness in this type of cycle as it is released in the pre-wash and lost on draining. The unwrapped single layer tablet thus perform more effectively in this respect for enzyme activity.

This problem associated with the unwrapped dual layer tablet is overcome by use of the water soluble wrapping which ensures that only a minor proportion of the enzyme is released during the prewash. Although the film was breached during the pre-wash it still gave considerable protection to the tablet during the pre-wash.

Although the unwrapped single layer tablet overcame the disadvantages of the unwrapped dual layer tablet with regard to enzyme activity, the wrapped dual layer tablet was superior to the unwrapped single layer tablet in relation to TAED, enzyme and perborate integrated activity.

The dual layer tablet was retarded in its dissolution due to the presence of the film. Despite this, the dual action gives an even better enzyme delivery in the wash than the single layer tablet since the activated bleach does not attach the enzyme. The incidental release of some material in the prewash may even be beneficial to reduce surface tension whereas releasing more (as in the other tablets) is simply wasteful.

Furthermore, the dissolved film will still be present until well into the rinses and (we have found) provides the advantage of acting as a rinse aid due to its ability to reduce surface tension in the incoming rinse water.

This is illustrated by the following test.

A glass slide was then placed in the dishwasher together with the wrapping material. The machine was operated, stopped during the second rinse cycle and a sample of the second rinse water taken. The slide was removed from the machine and

supported at an angle of 10°. The sampled rinse water was then squirted onto the slide from a wash bottle. The behaviour of the water on the slide was then observed.

The above procedure was repeated but using a conventional rinse aid (20ml of a 1% Synperonic LFRA (ex ICI) solution. The procedure was also repeated but without using any rinse aid or film.

The results are shown in the following table.

	De-wetting behaviour
No film or rinse aid	After 2 seconds the film breaks leaving some water droplets.
Rinse aid, as 20ml 1%, Synperonic LFRA 260 (ex ICI) solution.	Film drains evenly leaving occasional fine droplets.
Soluble film (Film No. 2 from Example 3)	Film drains evenly leaving occasional fine droplets.

As will be appreciated from the table, the soluble film provides wetting behaviour equivalent to that of the conventional rinse aid (Synperonic) and much improved (for the purposes of rinsing) compared to that obtained without film or rinse-aid. Thus, when using the wrapped tablet, there is no need to employ a separate rinse aid.

The soluble film also has the additional advantage of protecting the user from the materials of the formulation.

CLAIMS

1. A detergent tablet product for use in an automatic dishwashing machine, the product incorporating a tablet comprising first and second water soluble layers which are such that the former dissolves more rapidly than the latter under identical dissolution conditions, wherein said tablet is provided with a water soluble wrapping.

2. A product as claimed in claim 1 wherein the wrapping is of a film material comprised of polyvinyl acetate which has been at least partially hydrolysed to polyvinyl alcohol.

3. A product as claimed in claim 2 wherein the degree of hydrolysis is 50% to 100%.

4. A product as claimed in claim 3 wherein the degree of hydrolysis is 50% to 90%.

5. A product as claimed in claim 4 wherein the degree of hydrolysis is about 80%.

6. A product as claimed in any one of claims 1 to 5 wherein the wrapping has a thickness of 10 to 500 μm.

7. A product as claimed in claim 6 wherein said thickness is 30 to 200 μm.

8. A product as claimed in claim 7 wherein said thickness is 35 to 60 μm.

9. A product as claimed in any one of claims 1 to 8 wherein the film has a breach time of 10 to 300 seconds as measured by a test of the kind defined.

10. A product as claimed in claim 9 wherein the film has a breach time of 20 to 120 seconds as measured by a test of the kind defined.

11. A product as claimed in claim 10 wherein the film has a breach time of 20 to100 seconds as measured by a test of the kind defined.

12. A product as claimed in claim 11 wherein the film has a breach time of 30 to80 seconds as measured by a test of the kind defined.

13. A product as claimed in claim 12 wherein the film has a breach time of 30 to60 seconds as measured by a test of the kind defined.

14. A product as claimed in claim 13 wherein the film has a breach time of about 50 seconds as measured by a test of the kind defined.

15. A product as claimed in any one of claims 1 to 14 wherein the first layer of the tablet dissolves at least twice as rapidly as that of the second layer in water at a temperature of 55°C to 65°C.

16. A product as claimed in claim 15 wherein the first layer dissolves at least three times as quickly as the second layer.

17. A product as claimed in claim 15 or 16 wherein the first layer dissolves not more than four times as quickly as the second layer.

18. A product as claimed in any one of claims 1 to 17 wherein the water soluble film provides a rinse aid effect.

19. A product as claimed in any one of claims 1 to 18 wherein the first layer incorporates an enzyme and the second layer incorporates a bleach.

20. A method of producing a detergent tablet comprising co-compressing a first layer comprised of a light granular builder and a second layer comprised of a dense powdery builder to produce a tablet in which the first layer dissolves more rapidly in water than the second layer under identical dissolution conditions.

21. A method as claimed in claim 20 wherein the builder of the first layer, in its precompressed granular form has a bulk density of less than 0.8 g/cc and is such that at least 30% by weight would be retained on a 500 micron sieve and at least 15% by weight would be retained on a 710 micron sieve.

22. A method as claimed in claim 21 wherein said bulk density is less than 0.7 g/cc and the granulometry is such that at least 40% by weight would be retained on a 500 micron sieve and at least 25% by weight on a 710 micron sieve.

23. A method as claimed in claim 22 wherein said bulk density is less than 0.6 g/cc and the granulometry is such that at least 40% by weight would be retained on a 500 micron sieve and at least 25% by weight would be retained on a 710 micron sieve.

24. A method as claimed in any one of claims 1 to 23 wherein the builder of the second layer is such that, in its pre-compressed granular form, it has a bulk density greater than 0.8 g/cc and a granulometry such that less than 50% by weight would be retained on a 500 micron sieve and less than 30% by weight would be retained on a 710 micron sieve.

25. A method as claimed in claim 24 wherein the builder of the second layer is such that, in its pre-compressed granular form, it has a bulk density of greater than 0.9

g/cc and a granulometry such that less than 40% by weight would be retained on a 500 micron sieve and less than 20% by weight would be retained on a 710 micron sieve.

26. A method as claimed in claim 25 wherein the builder of the second layer is such that, in its pre-compressed granular form, it has a bulk density of greater than 1.0 g/cc and a granulometry such that less than 40% by weight would be retained on a 500 micron sieve and less than 20% by weight would be retained on a 710 micron sieve.

27. A method as claimed in any one of claims 20 to 26 wherein the builder of the first layer is an alkali metal polyphosphate, an alkali metal carbonate, alkali metal bicarbonate, zeolite or a crystalline or silicate builder system.

28. A method as claimed in any one of claims 20 to 27 wherein the tablet is compressed using a pressure of 20 to 500 MPa.

29. A method as claimed in claim 28 wherein said pressure is 50 to 350 MPa.

30. A method as claimed in claim 29 wherein said pressure is 80 to 200 MPa.

31. A method as claimed in any one of claims 20 to 30 wherein the builder of the second layer is an alkali metal polyphosphate, an alkali metal carbonate, alkali metal bicarbonate, zeolite or a crystalline or silicate builder system.

32. A method as claimed in any one of claims 20 to 31 wherein the builders of the first and second layers are chemically identical.

33. A method as claimed in claim 32 wherein the builder is sodium tripolyphosphate.

34. A method as claimed in any one of claims 20 to 33 wherein said first layer incorporates at least one enzyme.

35. A method as claimed in any one of claims 20 to 34 wherein the second layer incorporates an activated bleaching system.

36. A detergent tablet produced by the method of any one of claims 20 to 35.

37. A detergent tablet as claimed in claim 36 wherein the first layer incorporates at least one enzyme.

38. A detergent tablet as claimed in claim 36 or 37 wherein the second layer incorporates an activated bleaching system.

39. A pressed detergent tablet for use in an automatic dishwashing machine, the tablet comprising first and second water soluble layers which are such that the former dissolves more rapidly in water than the latter under identical dissolution conditions wherein the first layer incorporates an enzyme and a bleach and the second layer incorporates an activator for the bleach.

40. A tablet as claimed in claim 39 wherein each of the first and second layers comprise a builder, preferably providing a major proportion of each such layer.

41. A tablet as claimed in claim 40 wherein the builder of the first layer is an alkali metal polyphosphate, an alkali metal carbonate, alkali metal bicarbonate, zeolite or a crystalline or silicate builder system.

42. A tablet as claimed in claim 40 or 41 wherein the builder of the second layer is an alkali metal polyphosphate, an alkali metal carbonate, alkali metal bicarbonate, zeolite or a crystalline or silicate builder system.

43. A tablet as claimed in any one of claims 40 to 42 wherein the builders of the first and second layers are chemically identical.

44. A tablet as claimed in claim 43 wherein the builder is sodium tripolyphosphate.

45. A tablet as claimed in any one of claims 37, 38 (when dependent on claim 37) or 39 to 44 wherein the enzyme is at least one of a protease. amylase, oxidase, peroxidase or lipase.

46. A tablet as claimed in any one of claims 37 to 45 wherein the bleach of the first layer further is a compound which generates hydrogen peroxide on dissolution in water.

47. A tablet as claimed in claim 46 wherein the hydrogen peroxide precursor compound is a persalt.

48. A tablet as claimed in claim 47 wherein the persalt is a perborate. a percarbonate or a persulphate.

49. A tablet as claimed in any one of claims 39 to 48 wherein the bleach activator is a compound incorporating aliphatic acyl groups.

50. A tablet as claimed in claim 49 wherein the bleach activator is tetraacetylethylene diamine.

51. A tablet as claimed in claim 49 wherein the bleach activator is an acetylated sugar or sugar derivative.

52. A tablet as claimed in claim 51 wherein the bleach activator is acetylated sorbitol or acetylated mannitol.

53. A tablet as claimed in any one of claims 36 to 52 wherein the second layer incorporates a surface active agent.

54. A tablet as claimed in any one of claims 36 to 53 wherein the first layer dissolves at least twice as quickly as the second layer.

55. A tablet as claimed in claim 54 wherein the first layer dissolves at least three times as quickly as the second layer.

56. A tablet as claimed in any one of claims 36 to 55 wherein the first layer dissolves not more than four times as quickly as the second layer.

57. A detergent tablet product comprising a tablet as claimed in any one of claims 36 to 56 provided within a water soluble wrapping.

58. A detergent tablet product as claimed in any one of claims 1 to 18 wherein the tablet is as claimed in any one of claims 36 to 56.

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Claims searched:	1-19, 58	**Date of search:**	26 January 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q): C5D (DHE, DHZ, DDA, DJX)

Int Cl (Ed.6): C11D 17/00

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	EP0481547 A1	(Unilever) Examples 2 to 5	1 at least
X	WO92/20774 A1	(Ecolab) Examples 1 and 3	1 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.